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(54) Dialkyl perfluoro-omega-fluoroformyl diesters and monomers and polymers therefrom.

(57) Diesters of the formula:

$$(RO_2CCF_2)_2CFO(CFCF_2O)_nCFCOF$$
$$| \qquad\qquad |$$
$$CF_3 \qquad\quad CF_3$$
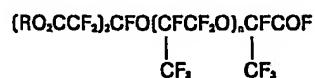
wherein R is CH_3 or C_2H_5 and n is 0 to 10; vinyl ether
monomers derived therefrom; copolymers of the vinyl
ether monomers with one or more selected perfluori-
nated monoolefins; articles of manufacture made from
the copolymers; process for making the diesters; pro-
cess for using copolymer membranes in a chlor-alkali
cell.

EP 0 048 964 A2

TITLE

DIALKYL PERFLUORO-ω-FLUOROFORMYL DIESTERS
AND MONOMERS AND POLYMERS THEREFROM

BACKGROUND OF THE INVENTION

5   This invention relates to dialkyl perfluoro-ω-fluoroformyl esters and to monomers and copolymers made therefrom. Following are descriptions of several background developments which provide a context in which to appreciate the present invention.

10   Krespan, in South African Patent 77/7158, disclosed $O=C(CF_2CO_2CH_3)_2$, perfluoroallyl ether dicarboxylates prepared therefrom and perfluorinated copolymers from said dicarboxylates. The perfluoroallyl ether dicarboxylates are neither homologs nor analogs of the perfluorovinyl ether dicarboxylates

15 described herein.

      Selman, in U.S. 3,274,239, disclosed fluoroketones of the formula, $XR_FC(O)R'_FX'$, where X and X' are H or halogen and R_F and R'_F are perfluoro-

20 alkylene of 1 to 8 carbon atoms; hexafluoropropene oxide (HFPO) adducts thereof,
$(XR_F)(X'R'_F)CFO(CF(CF_3)CF_2O)_nCF(CF_3)COF$, where n is 0 to 20; and vinyl ethers formed from said adducts.

      England, in U.S. 4,131,740, disclosed

25 the reaction of HFPO with a compound of the formula $FOC-CF_2-CO_2R$ in the presence of fluoride ion as catalyst and an inert liquid diluent (preferably an organic liquid) in which the selected fluoride is at least 0.001% soluble, to form alkyl perfluoro-ω-

30 fluoroformyl esters, $RO_2CCF_2(CF_2O(CF_3)CF)_nCOF$, where n is 0 to 6. Also disclosed are vinyl ethers formed from the esters, and perfluorinated copolymers of the vinyl ethers.

[CR 7986]

England, in U.S. 4,138,426, disclosed per-fluorovinyl ethers, $YCF_2(CF_2O(CF_3)CF)_pCF_2OCF=CF_2$, wherein Y is $-CO_2R$, $-CO_2H$, $-CO_2M$, or $-CN$; R is 1 to 6 carbons; M is alkali metal, ammonium or quaternary ammonium; and p is 1 to 5.

Breazeale, in U.S. Application Serial No. 083,751, filed October 22, 1979, disclosed vulcanizable copolymers of tetrafluoroethylene, perfluoromethyl perfluorovinyl ether and a cure site monomer consisting of a cyano-substituted perfluorovinyl ether of the formula, $CF_2=CF[OCF_2CF(CF_3)]_xO(CF_2)_nCN$, where n is 1 to 4 and x is 1 or 2.

SUMMARY OF THE INVENTION

This invention concerns dialkyl perfluor-ω-fluoroformyl diesters of the formula:

$$(RO_2CCF_2)_2CFO(\underset{\underset{CF_3}{|}}{C}FCF_2O)_n\underset{\underset{CF_3}{|}}{C}FCOF \qquad \underline{1}$$
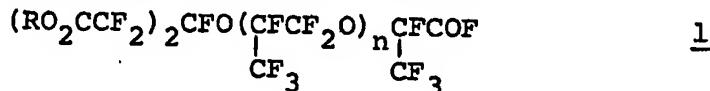
wherein R is CH_3 or C_2H_5 and n is an integer from 0 to 10.

This invention also concerns vinyl ethers derived from $\underline{1}$, said ethers having the formula:
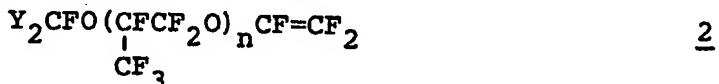
$$Y_2CFO(\underset{\underset{CF_3}{|}}{C}FCF_2O)_nCF=CF_2 \qquad \underline{2}$$

wherein Y is selected from the group CF_2CN, CF_2CO_2R, CF_2CO_2H, CF_2CO_2M, CF_2CONH_2 and CF_2CONR_2; R and n are as defined above; M is an alkali metal, ammonium or quaternary ammonium.

This invention also concerns copolymers of the vinyl ethers, $\underline{2}$, with one or more perfluorinated monoolefins selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, perfluoro-alkylvinyl ethers wherein the alkyl group contains 1 to 4 carbon atoms, chlorotrifluoroethylene, the vinyl ether, $CF_2=CF[OCF_2CF(CF_3)]_mOCF_2CF_2SO_2F$,

where m is 1 or 2, and mixtures thereof, said copolymers containing from about 0.1 to 80 mole percent of vinyl ether, $\underline{2}$. This invention also concerns articles of manufacture made from said copolymers,

5 including molded objects and ion-exchange membranes. This invention also concerns a process for producing an alkali metal hydroxide in a chlor-alkali electrolysis cell using an ion-exchange membrane prepared from said copolymers.

10 . This invention also concerns a process for preparing the diesters, $\underline{1}$, by contacting dialkyl-tetrafluoro-3-oxoglutarate, $O=C(CF_2CO_2R)_2$, $\underline{3}$, wherein R is CH_3 or C_2H_5, with hexafluoropropene oxide (HFPO), CF_2OCFCF_3, in the presence of fluoride ion as catalyst

15 and a solvent for reactants and catalyst.

DETAILS OF THE INVENTION

The Diester Adducts

. The dialkyl-tetrafluoro-3-oxoglutarate, $\underline{3}$, is reacted with HFPO in the presence of fluoride ion

20 as catalyst and a solvent. The fluoride ions are typically provided by one or more of the following sources: an alkali metal fluoride, an ammonium fluoride, a sulfonium fluoride such as benzene sulfonium fluoride and the like. Potassium fluoride

25 is preferred since its use results in improved product yields. The fluoride catalyst can be used in amounts of about 0.01 to 10 equivalents, preferably about 0.05 to 0.5 equivalents, per mole of $\underline{3}$.

Suitable solvents are aprotic liquids or

30 mixtures thereof, including the so-called glymes (mono-, di-, tri- and tetraethyleneglycol dimethyl ether); mononitriles such as aceto-, propio-, butyro- and benzonitrile; dinitriles such as malono-, succino-, glutaro-, adipo-, methylmalono-, pimelo-, subero-,

35 and phthalonitrile; nitrobenzenes; lactones such as γ-butyrolactone, δ-valerolactone and δ-caprolactone.

Preferred solvents are mixtures of dinitriles and glymes;
especially preferred are mixtures of adiponitrile
and tetraglyme in the proportion of about 80 to 98
weight percent of adiponitrile and 2 to 20 weight
5 percent of tetraglyme.

The reaction of ketone, 3, with HFPO is
exothermic. Reaction temperatures can range from
about 0° to 100°C, with temperatures between 25° and
70°C being preferred. Pressure is not critical,
10 and subatmospheric and superatmospheric pressures are
operable; pressures close to atmospheric are preferred.
As illustrated in the Examples, pressure in the
reaction vessel is normally controlled by regulating
the supply of gaseous HFPO.

15 Ketone, 3, is preferably present in substantial
excess at the beginning of the reaction. The ketone
reacts with 1 or more mols of HFPO to form adducts 1
in which n is 0 (1:1 monoadduct), or an integer of
1 to 10. Adducts wherein n=0 or 1 are preferred;
20 adducts wherein n=1 are most preferred. Use of excess
ketone, 3, in the reaction improves yields of the
desired lower adducts (n=0, 1) as well as overall
yields of adducts by suppressing formation of HFPO
oligomers which are undesired by-products formed by
25 fluoride ion-catalyzed polymerization of HFPO.

There are several reaction parameters which
affect the identity of the particular adduct that is
made. Because adduct solubility tends to decrease
in a given solvent as the value of n increases,
30 correspondingly better solvents are required to
dissolve adducts having high proportions of HFPO.
Also, relatively high temperatures and low HFPO
pressures (within the parameters described herein)
tend to favor production of adducts where n is at the
35 lower end of the range, 0 to 10. On the other hand,

alone or, preferably, in admixture with ketone, 3, as shown in Example 4. Such a mixture may be prepared by adding fresh ketone to the reaction vessel or by recovering the monoadduct and mixing it with a fresh charge of excess ketone and HFPO in a subsequent reaction. Other methods of assuring product optimization will be obvious to one skilled in the art from the description provided herein.

The Vinyl Ethers

The compounds for formula 1 can be pyrolyzed over a solid basic salt such as trisodium phosphate, potassium carbonate, or, preferably, sodium carbonate, to obtain the corresponding polymerizable vinyl ether monomers of formula 2':

$$(RO_2CCF_2)_2CFO(\underset{CF_3}{\underset{|}{C}}FCF_2O)_n\underset{CF_3}{\underset{|}{C}}FCOF \xrightarrow{\Delta}$$

1

$$(RO_2CCF_2)_2CFO(\underset{CF_3}{\underset{|}{C}}FCF_2O)_nCF=CF_2$$

2'
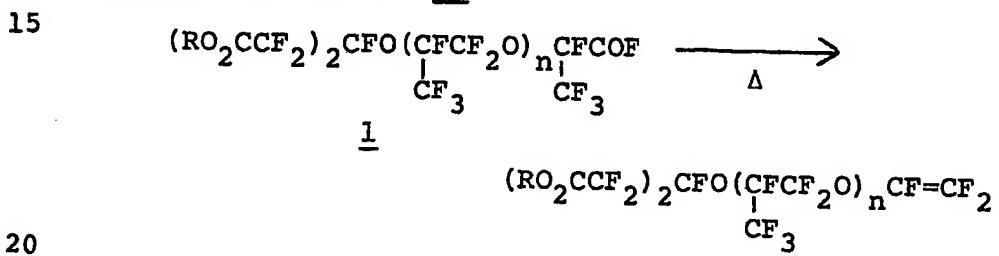
The pyrolysis reaction takes place at temperatures of about 120° to 300°C, preferably 150° to 250°C in an inert atmosphere, e.g., nitrogen, in the presence of the basic salts which have been previously dried by heating to at least 300°C. The monomeric diesters of formula 2' are converted by known methods into vinyl ether monomers having the following Y_2 values:

7

$$-CF(CF_2CO_2R)_2 \xrightarrow{\text{H}_2\text{O}/\text{H}^+} -CF(CF_2CO_2H)_2$$

$$-CF(CF_2CO_2R)_2 \xrightarrow{\text{NH}_3} -CF(CF_2CONH_2)_2$$

5

$$-CF(CF_2CONH_2)_2 \xrightarrow{-\text{H}_2\text{O}} -CF(CF_2CN)_2$$

$$-CF(CF_2CO_2R)_2 \xrightarrow{\text{NHR}_2} -CF(CF_2CONR_2)_2$$

10

$$-CF(CF_2CO_2R)_2 \xrightarrow{\text{MOH}} -CF(CF_2CO_2M)_2$$
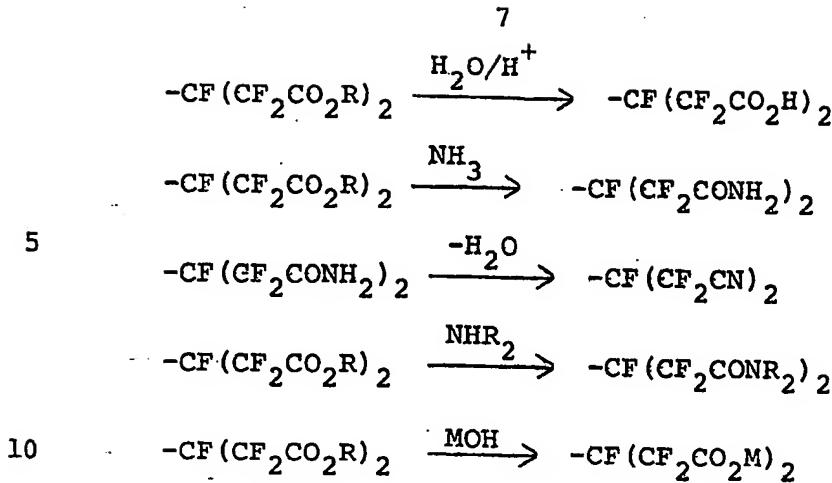
wherein R and M are as previously defined.

Monomers of formula 2 can be copolymerized
with one or more of the fluorinated vinyl monomers
listed above (tetrafluoroethylene, etc.) to yield solid,
15 tough thermoplastic copolymers which can be molded into
shaped articles, including films, and ion exchange
membranes for chloralkali electrolysis cells. Alter-
natively, for polymer uses requiring ion-exchange
capability, the monomer, 2', can be copolymerized
20 with said fluorinated vinyl monomers and the copolymer
subsequently converted by hydrolysis to the corres-
ponding copolymer containing $-CF_2CO_2H$ or $-CF_2CO_2M$
groups. Formula 2 monomers wherein Y is $-CF_2CN$ are
especially useful for incorporating cure sites into
25 fluoroelastomer compositions.

It will be understood that the vinyl monomers
of this invention contain two especially useful terminal
functional groups in addition to the polymerizable
vinyl site. Thus, the present monomers make it possible
30 to double the functionality of copolymers derived
therefrom without increasing the molar percentage of

functional monomers in said copolymers. Alternatively, copolymer functionality can be maintained while only employing half the molar percentage of functional monomer previously necessary.

5   Copolymers

Copolymers prepared from Formula $\underline{2}$ vinyl monomers contain repeating units having the formula

$$-CF-CF_2[CXCX_2]_q[CFCF_2]_r$$
$$\quad|\qquad\qquad|\qquad\quad Z\qquad\qquad[OCF_2CF(CF_3)]_mOCF_2CF_2SO_2F$$

10   $[OCF_2CF(CF_3)]_nOCFY_2$
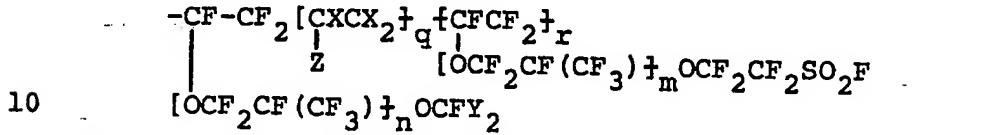
where Y and n are as defined above, m is 1 or 2, q is about 1 to 500, r is 0 or about 1 to 5, Z is $-F$, $-R_F$ or $-OR_F$ where R_F is perfluoroalkyl of 1 to 6 carbon atoms, preferably 1 or 2 carbon atoms, and

15   the X's can all be fluorine or two can be fluorine and one chlorine. Preferred copolymers are those wherein X and Z are $-F$, Y is $-CF_2CO_2R$ or $-CF_2CN$, n is 1 or 2, q is 3 to 500, r is 0 or 1 and m is 1. Values of q from 3 to 20 are preferred for carboxylated

20   copolymers used as electrolysis cell membranes; q of 40 to 400 and r = 0 are preferred in nitrile-functional fluoroelastomers. Preferred monoolefins for copolymerization with formula $\underline{2}$ vinyl ethers include tetrafluoroethylene, hexafluoropropylene,

25   perfluoroalkylvinyl ethers wherein the alkyl group contains 1 to 4 carbon atoms, chlorotrifluoro-ethylene, the vinyl ether, $CF_2=CF[OCF_2CF(CF_3)]_mOCF_2CF_2SO_2F$, where m is 1 or 2, and mixtures thereof.

30   In the following Examples parts are by weight unless otherwise specified. Temperatures are in degrees Centrigrade.

35

EXAMPLE 1
Reaction of Dimethyl
Tetrafluoro-3-Oxyglutarate
With Hexafluoropropene Oxide

5   Cesium fluoride (10 g, 0.18 mol) in a 2
liter 3-neck flask was heated by a Meker burner under
vacuum with swirling to dryness. After cooling, the
flask was filled with nitrogen and fitted with a
thermometer and large magnetic stirrer. Then, 15 ml
10 of tetraglyme and 19.5 g (0.08 mol) of the above
titled ketoester were added. The flask was evacuated
and then automatically maintained at about 700 mm (91
kPa) pressure of HFPO. Vigorous stirring resulted in
exothermic (54°) absorption of HFPO which was arbitrarily
15 stopped after 19 g (0.11 mol) had been absorbed.
Two liquid layers were present in the reaction
mixture after HFPO absorption, indicating reaction
products which were insoluble in tetraglyme.

     Vacuum (ca. 1.0 mm, 130 Pa) was applied to
20 the flask through a liquid nitrogen-cooled trap while
heating the flask with steam. The contents of the trap
were distilled and fractions collected boiling from
30°/15 mm (2 kPa) to 82°/0.2 mm (26 Pa). The higher
boiling fractions contained two layers due to co-
25 distillation of tetraglyme. The fractions are believed
to have contained adducts, 1, wherein n = 0 to 10.
By-product HFPO oligomers formed, if any, were present
in lower boiling fractions not collected.

EXAMPLE 2

30    $(CH_3OOCCF_2)_2C=O$ + $\underset{\underset{O}{\diagdown\diagup}}{CF_2-CF-CF_3}$ $\longrightarrow$

$$(CH_3OOCCF_2)_2CFO(CFCF_2O)_n CFCOF$$
$$\qquad\qquad\qquad\quad \overset{CF_3}{|} \qquad \overset{CF_3}{|}$$
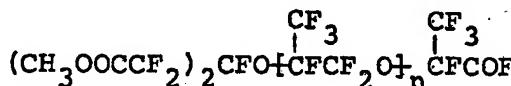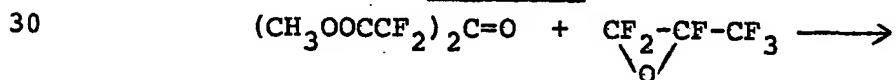
35   Potassium fluoride (5 g, 0.09 mol) in a 2
liter 3-neck flask was heated by a Meker burner under

vacuum with swirling to dryness. After cooling, the
flask was filled with nitrogen and fitted with a
thermometer and large magnetic stirrer. Then, 2.54 g
of tetraglyme (bis[2-(2-methoxyethoxy)ethyl]ether)

5   and 40 ml (48.5 g) of adiponitrile were added, the
flask evacuated and flushed again with nitrogen.
Dimethyl tetrafluoro 3-oxoglutarate (MKG) (321 g,
1.3 mol) was added and the flask evacuated, filled
with HFPO and weighed. Stirring was started and after

10 an induction period of about one hour absorption of
HFPO began, reaching a maximum of about 0.6 g/min and
a temperature of 37°. HFPO pressure was automatically
maintained at about 700 mm (91 kPa). The flask was
weighed periodically and addition of HFPO was stopped

15 arbitrarily after 267 g (1.6 mol) had been absorbed.
The contents of the flask were filtered
through a sintered glass funnel to remove KF and the
filtrate was distilled under vacuum (0.5-1.0 mm; 65 to
130 Pa). There was recovered 79.5 g of HFPO oligomers

20 (mostly dimer and trimer) from the Dry Ice-cooled trap
on the still and as bottom layer in the first cuts of
recovered MKG. The first cuts boiling up to 78°/0.8
mm (104 Pa) after removing bottom layer amounted to
378 g and were about 50 mol percent of MKG and 50 mol

25 percent (237 g) of monoadduct (n = 0), dimethyl
2,2,3,4,4-pentafluoro-3-(1-fluorocarbonyl-1,2,2,2-
tetrafluoroethoxy)pentanedioate, as analyzed by gas
chromatography.
There was then obtained 8.6 g of diadduct

30 (n = 1), dimethyl 2,2,3,4,4-pentafluoro-3-[2-(1-fluoro-
carbonyl-1,2,2,2-tetrafluoroethoxy)-1,2,2-trifluoro-
1-(trifluoromethyl)ethoxyl]-pentanediolate, b.p.
86°/1 mm (130 Pa); 12.7 g of triadduct (n = 2) dimethyl
2,2,3,4,4-pentafluoro-3-[2,3,3,5,6,6,8,9,9,9,-decafluoro-

35 8-fluorocarbonyl-2,5-bis(trifluoromethyl)-1,4,7-tri-
oxanon-1-yl]pentanedioate, b.p. 93°/0.4 mm (52 Pa);

11 ʼ

9.0 g of tetraadduct (n = 3),.dimethyl 2,2,3,4,4-
pentafluoro-3-[2,3,3,5,6,6,8,9,9,11,12,12,12-trideca-
fluoro-11-fluorocarbonyl-2,5,8-tris(trifluoromethyl)-
1,4,7,10-tetraoxanon-1-yl]pentanedioate, b.p. 103°/0.4 mm

5   (52 Pa) and 150 g of higher boiling material including
adiponitrile. The adiponitrile began to codistill with
the adduct and separated from these fractions as a top
layer which was removed before the next step. Analytical
data and physical properties of the HFPO adducts (n =

10 1,2,3,4) are given in Tables 1 and 2.

EXAMPLE 3

Dimethyl tetrafluoro-3-oxoglutarate (MKG)
(124 g, 0.5 mol) was reacted with HFPO as described in
Example 2 using 60 ml of diglyme as solvent and 10 g

15 of cesium fluoride plus 3.5 g of potassium fluoride as
catalyst. Reaction was exothermic (53°) after an
induction period of 2.5 hrs. However, the HFPO absorbed
(1099 g, 6.62 mol) was largely converted to HFPO
oligomers. There was isolated 45 g of the monoadduct

20 (n = 0), b.p. 73°/1.4 mm (182 Pa). Physical and
analytical data for the monoadduct are given in Tables
1 and 2.

EXAMPLE 4

A mixture of dimethyl tetrafluoro-3-oxo-
25 glutarate (MKG) (50 g, 0.2 mol) and its mono-HFPO
adduct (50 g, 0.12 mol) were reacted with excess HFPO
using 5 g of KF as catalyst and a mixture of 50 g of
adiponitrile and 2.6 g of tetraglyme as solvent. After
55 g (0.33 mol) of HFPO had been absorbed the mixture
30 consisted of two layers. The bottom layer was removed
and distilled to give about 52 g of a mixture of 8 mol
percent of MKG and 92 mol percent (49 g) of monoadduct
(n = 0); 11 g of diadduct (n = 1); and 14 g of triadduct
(n = 2).

12

The reaction was restarted after adding 102 g (0.41 mol) of MKG to the top layer and was stopped after absorbing 203 g (1.22 mol) of HFPO. Two layers were again formed. Distillation of the lower layer gave

5   83 g of a mixture of 2 mol percent of MKG and 98 mol percent (81 g) of monoadduct; 27 g of diadduct; and 45 g of triadduct.

EXAMPLE 5

10

$$(CF_3OOCCF_2)_2CFO\{CFCF_2O\}_n\overset{CF_3}{CF}COF \longrightarrow$$

$$(CH_3OOCCF_2)_2CFO\{CFCF_2O\}_n\overset{CF_3}{CF}=CF_2$$
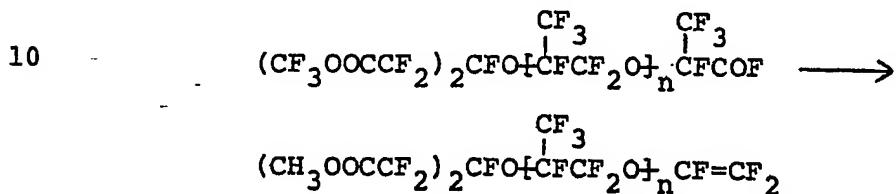
An acid fluoride of the above formula (n = 1,

15 33 ml, 49 g, 0.085 mol) prepared as in Example 2, was added through a syringe driven by a Sage pump at the rate of 0.6 ml/min to a stirred bed of 90 ml of sodium carbonate at 190° (previously dried at 400°) under a slow current of nitrogen. The sodium carbonate was

20 contained in a quartz tube, 2.54 cm diameter x 45.7 cm long, fitted at the top with openings for nitrogen, syringe needle and a motor driven screw running through the bed and heated by a split-type furnace. Product was collected at the bottom of the tube.

25   When addition was complete, vacuum was applied and there was collected in Dry-Ice – and liquid nitrogen – cooled traps (in series) 38.5 g of material. Distillation gave 23 g of the above vinyl ether (n = 1), dimethyl 2,2,3,4,4-pentafluoro-3-[2-(1,2,2-trifluoro-

30 ethenyloxy)-1,2,2-trifluoro-1-(trifluoromethyl)-ethoxy]pentanedioate, b.p. 77°/0.1 mm (13 Pa). Higher boiling cuts showed the presence of some decarboxylation product [$CF(CF_3)H$] in place of $CF=CF_2$ in the above formula]. Physical and analytical data for the vinyl

35 ether are given in Tables 1 and 2.

13

EXAMPLE 6

$$(CH_3OOCCF_2)_2CFO \left[\begin{matrix} CF_3 \\ | \\ CFCF_2O \end{matrix} \right]_n \begin{matrix} CF_3 \\ | \\ CFCOF \end{matrix} \longrightarrow$$

$$(CH_3OOCCF_2)_2CFO \left[\begin{matrix} CF_3 \\ | \\ CFCF_2O \end{matrix} \right]_n CF=CF_2$$
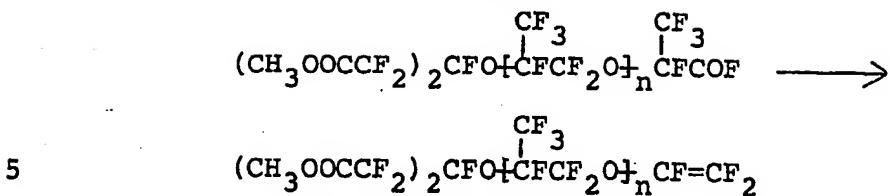
An acid fluoride of the above formula
(n = 2, 20 ml, 34.5 g, .046 mol), prepared as in
Example 2, was passed through a stirred bed of 90 ml
of sodium carbonate at 202° as described in Example 4.
In the same way, 22.5 g was recovered giving on dis-
tillation 12 g of the vinyl ether (n = 2), dimethyl
2,2,3,4,4-pentafluoro3[2,3,3,5,6,6,8,9,9-nonafluoro-
2,5-bis(trifluoromethyl)-1,4,7-trioxa-8-nonen-1-yl]-
pentanedioate, b.p. 87°/0.1 mm (13 Pa). Physical
and analytical data for the vinyl ether are given in
Tables 1 and 2.

A higher-boiling impurity was largely the
decarboxylation product ($CF(CF_3)H$ in place of $CF=CF_2$).

EXAMPLE 7

Preparation and Hydrolysis of Copolymer

$$(CH_3OOCCF_2)_2CFO\text{-}\begin{matrix}CF_3\\|\\CFCF_2\end{matrix}OCF\left[CF_2\text{-}CF_2\right]_q$$
$$|$$
$$CF_2$$
$$|$$

$$NaOH \downarrow$$

$$(NaOOCCF_2)_2CFO\text{-}\begin{matrix}CF_3\\|\\CF\end{matrix}\text{-}CF_2OCF\left[CF_2\text{-}CF_2\right]_q$$
$$|$$
$$CF_2$$
$$|$$
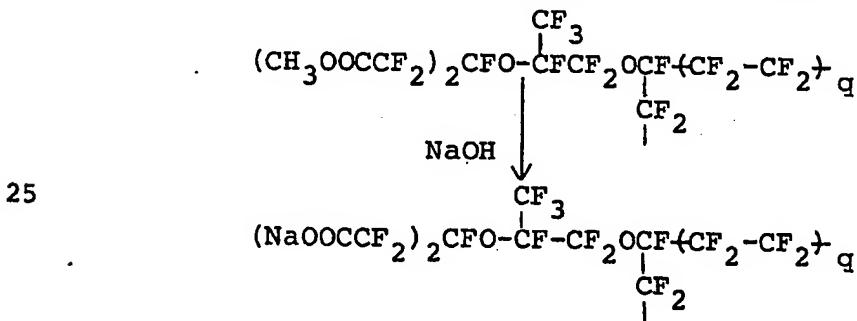
The vinyl ether monomer prepared in Example 5
(n = 1, 10.2 g, 0.02 mol), 17.3 g of 1,1,2-trichloro-
1,2,2-trifluoroethane (F-113) (distilled under nitrogen),
2.8 g of (0.028 mol) tetrafluoroethylene and 40 μl of
perfluoropropionyl peroxide solution (6% in F-113)
were sealed in a 20 ml Carius tube (nearly full).
After rotating the tube at room temperature overnight
the polymer was rinsed out and washed on a sintered

glass funnel with F-113, pressure filtered with nitrogen and vacuum dried in a steam bath to give 1.7 g of white solid. A 7 mil film was pressed at 180° and 5 to 6 mil (0.13-0.15 mm) film at 200°/500 psi (3435 kPa).

5 Infrared spectroscopy of the film showed strong ester carbonyl absorption at 5.6 microns. Infrared spectroscopy of a film removed from aluminum foil by boiling in 10% sodium hydroxide showed broad and strong absorption at 2.9 microns and 5.9 microns for COONa.

10 Vinyl ether monomer was recovered from the above F-113 solution and redistilled. A Carius tube charge of 8.9 g of vinyl ether, 19.7 g of F 113, 3.4 g of tetrafluoroethylene and 40 µl of perfluoropropionyl peroxide solution treated as above gave 3.2 g of

15 copolymer from which a 7 mil (0.18 mm) film was pressed at 220°/500 psi (3435 kPa).

EXAMPLE 8

In a run similar to that of Example 2, starting with 447 g of a mixture of MKG (35 mol

20 percent) and monoadduct (65 mol percent) recovered from Example 2, in which 90 g of HFPO was absorbed, there was obtained 35 g of HFPO oligomers, 401 g of starting mixture of MKG and monoadduct (35 mol percent of MKG, 65 mol percent of monoadduct (303 g)), 18.1 g

25 of diadduct, 11.4 g of triadduct (n = 2), 10.3 g of tetraadduct (n = 3) and 92.5 g of higher-boiling material including adiponitrile.

EXAMPLE 9

Potassium fluoride (1.4 g, 0.024 mol) was

30 placed in a 125 ml round-bottom flask fitted with a magnetic stirrer, dropping funnel, Dry ice-cooled condenser and nitrogen inlet, and "flamed out" under nitrogen with a heat gun. After cooling to 28°, 28.4 g of anhydrous diglyme was added to the flask,

35 followed by slow addition, with stirring, of dimethyl

tetrafluoro-3-oxoglutarate (MKG) (29.5 g, 0.12 mol)
during which the temperature rose to 33°. Stirring
was continued for 1 h after MKG addition was completed.
Almost all the KF dissolved. The flask was evacuated,
5   then filled with 37 g (0.223 mol) of hexafluoro-
propene oxide (HFPO). Reaction proceeded at or
below 35° for 1.5 h. The reaction mixture, which
consisted of two liquid layers, was stirred overnight
at room temperature.

10   The two layers were separated and weighed:
total weight, 89.9 g; lower layer, 26.5 g, upper
layer, 63.4 g. Vacuum distillation of the upper
layer gave two fractions boiling at (1) 84° to 85°/
50 mm (29.9 g) and (2) 85° to 90°/10 mm (23.8 g).
15   Gas chromatography, infrared and nuclear magnetic
resonance analysis showed fraction (1) to be largely
diglyme, and fraction (2) to contain the monoadduct
$(CH_3OOCCF_2)_2CFOCFCOF.$
$$\overset{|}{C}F_3$$

20   EXAMPLE 10
          Potassium fluoride, (5.0 g, 0.09 mol) was
added to a 125 ml flask fitted as described in
Example 9 and heated under nitrogen. Butyrolactone
(45.0 g) and dimethyl tetrafluoro-3-oxoglutarate (MKG)
25   (22.4 g, 0.091 mol) were then added, with stirring,
followed by hexafluoropropene oxide (HFPO) (26.0 g,
0.157 mol). Moderately rapid reaction occurred and
the temperature rose to 30° to 40°. The reaction
mixture consisted of solids and two liquid layers.
30   The solids were filtered off and the liquid layers
were separated and weighed: total liquid weight,
89.0 g; lower layer, 65.6 g, upper layer, 23.4 g.
Gas chromatographic analysis showed that the lower
layer contained unreacted MKG, butyrolactone, HFPO
35   oligomers and compounds of the formula

16

$(CH_3O_2CCF_2)_2CFO[CFCF_2O]_n CFCOF$ where $n = 0, 1, 2$
$\qquad\qquad\qquad\qquad\quad CF_3$
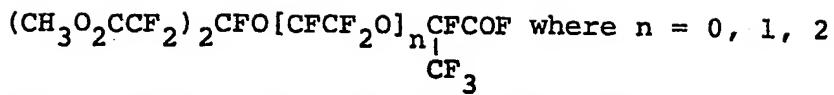
and 3 (mono-, di-, tri- and tetraadducts).

EXAMPLE 11

5
$$-CF-CF_2[CF_2CF_2]_q$$
$$OCF_2CF(CF_3)OCF(CF_2CO_2CH_3)_2$$
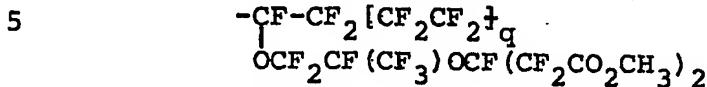
The vinyl ether prepared as in Example 5
(n = 1; 16.0 g, 0.031 mol), 1,1,2-trichloro-1,2,2-
trifluoroethane (23.5 g), Percadox 16 (bis[4-t-butyl-
10 cyclohexyl]peroxydicarbonate, Noury Chemical Co.;
0.05 g) and tetrafluoroethylene (about 20 g, 0.20
mol) were heated in a stainless steel tube at 45°
(4 h), 50° (30 min) and 55° (30 min). The colorless/
milky polymeric gel product was washed three times
15 with acetone, filtered and dried in a vacuum oven.
The white product weighed 110.1 g. A 2.4 mil film
was pressed at 225° from which an infrared spectrum
was obtained consistent with that of a copolymer of
the above structure.

20 The copolymer had an equivalent weight of
746 as determined by nuclear magnetic resonance in
the following manner at 275°. Signals were obtained
in the -79 ppm region, the -115 to -120 ppm region and
the -134 ppm region using a CCl_3F standard corres-
25 ponding to the CF_2O/CF_3 groups, CF groups and OCF
groups, respectively. The integrals were 19.0 for
the -79 ppm region (CF_2O/CF_3) and 187.5 for the rest
of the spectrum. The equivalent weight of the polymer
was calculated as follows.

30 Each comonomer unit contains 5 fluorine
atoms in CF_2O or CF_3 groups, (a). Thus, each fluorine
is equal to 19.0/5=3.8 integral units. The rest of
the polymer contains 187.5 integral units arising
from other comonomer fluorine atoms and fluorine
35 atoms originally found in tetrafluoroethylene, (TFE).

The remaining nine fluorine atoms from the comonomer,
(b), are equal to 9 x 3.8=34.2 integral units. The
fluorine atoms arising from TFE are equal to 187.5-
34.2=153.3 integral units while those from the

5   comonomer are equal to 34.2+19=53.2 integral units.
Therefore, the molar ratio of TFE to comonomer equals

$$\frac{153.3/4}{53.2/14} = \frac{38.3}{3.8}$$

or 5.04 moles of TFE per 0.5 mole of comonomer. Since

10 the molecular weight of the comonomer is 484 as the
free dicarboxylic acid, the equivalent weight =
5.04 (100) + 484 (.5) = 746 (or 1.34 meq H^+/g).
Thus, q in the above formula is 10 (5.04 x 2).

EXAMPLE 12

15   Vinyl ethers, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$,
(18.9 g, 0.042 mol), $CF_2=CF[OCF_2CF(CF_3)]_2OCF(CF_2CO_2CH_3)_2$
prepared as in Example 6 (11.2 g, 0.028 mol),
Percadox 16 (Noury Chemical Co., 0.05 g), 1,1,2-
trichloro-1,2,2-trifluoroethane (46.9 g) and tetra-

20 fluoroethylene (about 24 g, 0.24 mol) were heated in
a stainless steel tube as described in Example 11.
The white polymer product, after washing in acetone,
filtering and drying, weighed 23.4 g. A clear film
was pressed between Teflon® plates at 250°. Its

25 infrared spectrum was consistent with that of a
terpolymer of the above vinyl ethers and tetra-
fluoroethylene.

UTILITY

        An ion-exchange resin of the copolymer of

30 Example 11 in film form was prepared as follows:
2.0 g of the copolymer, 50 ml of methanol and 7.5 g
of potassium hydroxide were placed in a 100 ml round
bottom flask fitted with a magnetic stirrer and
water-cooled condenser and heated to reflux under

35 nitrogen for 16 h. The flask was then cooled and

a gel-like polymer was collected by filtration, washed thoroughly with anhydrous methanol and dried in a vacuum oven. Analysis showed that the polymer was in the form of its potassium (alkali metal) salt.

5   A film of the polymer, pressed at 250°C, was clear.

The carboxyl-functional perfluorinated copolymers of this invention are contemplated for use as cation exchange membranes in chlor-alkali cells. For that utility, the carboxyl-containing

10   membranes would be hydrolyzed to convert the carboxyl groups to the sodium (alkali metal) salt form. In their sodium salt form, the membranes would perform their essential function of permitting migration of sodium cations from the anode compartment to

15   the cathode compartment while preventing the migration of chloride ions from the anode compartment to the cathode compartment.

Vinyl ether monomers of this invention are useful in the vulcanization of fluoroelastomers.

20   Copolymerization of vinyl ether monomers of formula 2 wherein Y is CF_2CN with selected perfluorinated monomers such as TFE and perfluoromethylvinyl ether provides curable copolymers which, when heated in the presence of substances known to promote the

25   formation of triazine rings by trimerization of nitriles, become cured (vulcanized) fluoro-elastomers.

TABLE 1

INFRARED, BOILING POINT AND ANALYTICAL DATA

A.

$$CH_3OOCCF_2 \diagdown \quad F$$
$$\qquad\qquad C \diagup \quad CF_3 \qquad\qquad CF_3$$
$$CH_3OOCCF_2 \diagup \quad \diagdown O[CF-CF_2O]_n CFCOF$$
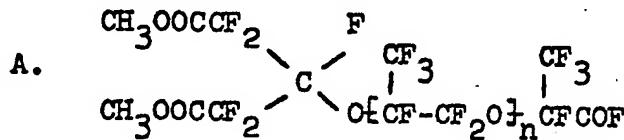
Ex.	n	Infrared wave length microns		Boiling Point °C/mm (Pa)	Refractive Index n_D^{25}
		F C=O	OCH_3 C=O		
3	0	5.30	5.55	73/1.4(182)	1.3468
2	1	5.30	5.55	86/1.0(130)	1.3370
2	2	5.30	5.55	93/0.4(52)	1.3287
2	3	5.30	5.55	103/0.4(52)	1.3230

Analyses

Ex.	Calculated			Found			Formula
	C	H	F	C	H	F	
3	29.14	1.47	46.10	29.25	1.80	46.09	$C_{10}H_6F_{10}O_6$
2	27.00	1.05	52.58	27.96	1.47	52.49	$C_{13}H_6F_{16}O_7$
2	25.82	0.81	56.17	26.69	0.93	56.27	$C_{16}H_6F_{22}O_8$
2	25.07	0.66	58.44	24.99	0.89	59.43	$C_{19}H_6F_{28}O_9$

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20

TABLE 1 (CONTINUED)

INFRARED, BOILING POINT AND ANALYTICAL DATA

5   B.

$$CH_3OOCCF_2 \diagdown C \diagup{}^F \atop \diagdown O[CF-CF_2O]_n CF=CF_2 \atop CH_3OOCCF_2 \diagup$$ CF_3

10
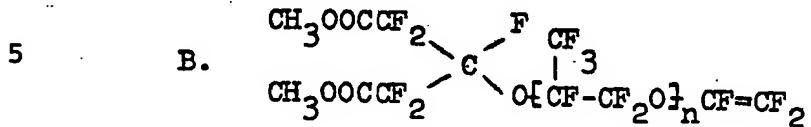
Ex.	n	Infrared wave length microns		Boiling Point °C/mm (Pa)	Neut. Equiv. of Acid
		F C=O	OCH$_3$ C=O		
4	1	5.40	5.55	77/0.1(13)	242
5	2	5.38	5.55	87/0.1(13)	325

15

Analyses

Ex.	Calculated			Found			Formula	Mol Wt
	C	H	F	C	H	F		
4	28.14	1.18	51.94	28.78	1.43	51.87	$C_{12}H_6F_{14}O_6$	512
5	26.56	0.89	56.03	26.54	1.02	56.12	$C_{15}H_6F_{20}O_7$	678

20

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA

Proton magnetic resonance spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as external standard with downfield direction taken as positive. ^{19}F magnetic resonance spectra were obtained with a Varian A 56/60 spectrometer operating at 56.4 MHz; chemical shifts are reported.

A.

$$CH_3OOCCF_2 \diagdown \diagup F$$
$$C$$
$$CH_3OOCCF_2 \diagup \diagdown O[CFCF_2O]_n CFCOF$$
$$\overset{\displaystyle CF_3}{\underset{}{}} \quad \overset{\displaystyle CF_3}{\underset{}{}}$$

Chemical Shifts δ ppm

Ex.	n	CH$_3$	COF	CF$_3$	CF$_2$O	CF$_2$(4F)	CF
3	0	3.70	+26.98	-82.16		-115.80	-124.86
							-138.85
2	1	3.70	+26.57	-79.18	-79(1F) broad	-115.84	-130.55
				-82.15	-85(1F) broad		-135.59
							-138.14
2	2	3.67	+26.41	-79.21	-79(2F) broad	-115.83	-130.59
				-80.09	-85(2F) broad		-135.46
				-82.28			-138.01
							-145.04
2	3	3.65	+26.30	-79.33	-79(3F) broad	-115.91	-130.73
				-80.17 (6F)	-85(3F) broad		-135.48
				-82.37			-138.73
							-144.91(2F)

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TABLE 2 (CONTINUED)

NUCLEAR MAGNETIC RESONANCE DATA

</div>

5   B.

$$CH_3OOCCF_2 \diagdown \quad F$$
$$C$$
$$CH_3OOCCF_2 \diagup \quad CF_3$$
$$O(CFCF_2O)_n CF=CF_2$$
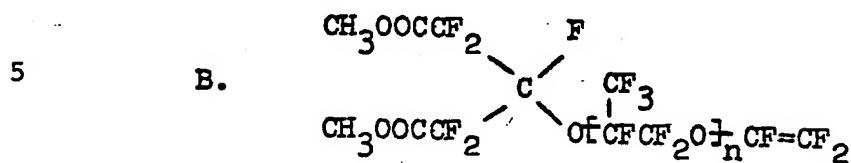
| Ex.	n	Chemical Shifts δ ppm					Coupling constants for CF J_{FF} in Hz
		CH_3	CF_3	CF_2O	$CF_2(4F)$	CF	
4	1	3.68	-79.32	-84.06	-115.93	-114.68	85.6(d), 65.6(d)
						-122.47	112(d), 85.6(d), 6.2(t)
						-136.12	112(d), 65.6(d) 6.2(t)
						-138.35	
						-135.30	
5	2	3.68	-79.20	-79.48	-115.81	-114.55	86.8(d), 66.8(d), 6.2(d)
			-80.14	-84.69		-122.41	111(d), 86.8(d), 6.0(t)
						-136.35	111(d), 66.8(d), 4.0(t), 2.0(d)
						-135.25	
						-138.18	

CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

5   1.   A diester of the formula:

$$(RO_2CCF_2)_2CFO(CFCF_2O)_nCFCOF$$
$$\qquad\qquad\qquad CF_3 \qquad CF_3$$
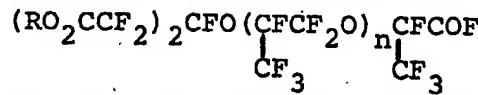
wherein R is CH_3 or C_2H_5 and n is an integer from 0 to 10.

10   2.   A diester according to Claim 1 wherein n is 0 or 1.

3.   A vinyl ether monomer of the formula:

$$Y_2CFO(CFCF_2O)_nCF{=}CF_2$$
$$\qquad\qquad CF_3$$
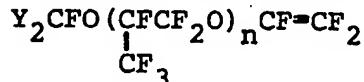
15 wherein Y is selected from the group CF_2CN, CF_2CO_2R, CF_2CO_2H, CF_2CO_2M, CF_2CONH_2 and CF_2CONR_2; R is CH_3 or C_2H_5; n is an integer from 0 to 10; M is an alkali metal, ammonium or quaternary ammonium group.

4.   A vinyl ether monomer according to Claim 3
20 wherein n is 0 or 1.

5.   A vinyl ether monomer according to Claim 4 wherein Y is CF_2CO_2R or CF_2CN.

6.   A copolymer of the monomer according to Claim 3 and at least one perfluorinated comonomer
25 selected from the group consisting of tetrafluoro-ethylene, hexafluoropropylene, chlorotrifluoroethylene, perfluoroalkylvinyl ether wherein the alkyl group contains 1 to 4 carbon atoms, and the vinyl ether, $CF_2{=}CF(OCF_2CF(CF_3))_mOCF_2CF_2SO_2F$, where m is 1 or 2.

30   7.   A copolymer according to Claim 6 comprising repeating units of the formula:

$$-CFCF_2(CXCX_2)_q(CFCF_2)_r$$
$$\quad|\qquad\;\; |\qquad\qquad\;\; |$$
$$\quad|\qquad\;\; Z\qquad\quad (OCF_2CF(CF_3))_mOCF_2CF_2SO_2F$$
$$(OCF_2CF(CF_3))_nOCFY_2$$

35
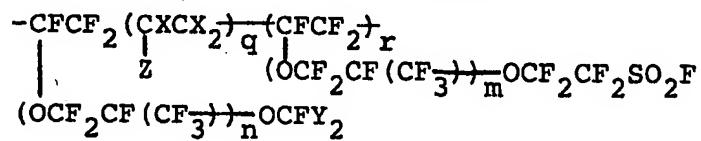
wherein q is about 1 to 500, r is 0 or an integer
of 1 to 5, m is 1 or 2, Z is $-F, -R_F$ or $-OR_F$, R_F
is perfluoroalkyl of 1 to 4 carbon atoms, and the 3
X's are each fluorine or two are fluorine and one is
chlorine.

8. A copolymer according to Claim 7 wherein
each X and Z is F, Y is CF_2CO_2R or CF_2CN, n is 1 or 2,
q is 3 to 500 and r is 0 or 1.

9. A process for producing alkali metal
hydroxide comprising reacting alkali metal chloride and
water in an ion exchange membrane-containing chlor-
alkali electrolysis cell characterized by employing
in said cell an ion-exchange membrane formed from the
copolymer of Claim 6.

10. An ion exchange membrane-containing
chloralkali electrolysis cell characterized by having
an ion-exchange membrane formed from the copolymer of
Claim 6.

11. A process for making the diester according
to Claim 1 comprising reacting

$$(RO_2CCF_2)_2C=O$$

with hexafluoropropene oxide in the presence of
fluoride ion catalyst and an aprotic solvent.